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(54) PRINTING INK FOR METAL

(57)Abstract:

PURPOSE: To provide a printing ink for a metal, excellent in printing properties and capable of forming a coating film excellent in physical properties in the method for printing a metal where a wet-coating of an aqueous overprint varnish is applied after printing with an ink.

CONSTITUTION: In relation to a printing ink for a metal, composed mainly of a resin, a pigment and a solvent, this invented printing ink for a metal contains a polyester synthesized from a polyol component composed of an alkylene oxide adduct of a compound having two or more active hydrogens or an alkylene oxide adduct of bisphenol or an aliphatic polyvalent alcohol and a polycarboxylic acid and an amino resin as the resin components.

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CLAIMS

[Claim(s)]

[Claim 1] Printing ink for metals which uses the polyol component which consists of an alkylene oxide addition product (a) of the compound which has two or more active hydrogen as this resinous principle in the printing ink for metals which changes considering resin, a pigment, and a solvent as a principal component, the polyester (A) from carboxylic acids (b), and amino resin (B), and is characterized by the content of (A) to the whole quantity of printing ink being 10 - 70 % of the weight (I).

[Claim 2] Printing ink according to claim 1 whose (A) is polyester of hydroxyl values 30-300 (I).

[Claim 3] Printing ink according to claim 1 or 2 whose (a) is the ethylene oxide of the alcohols more than trivalent [of carbon numbers 3-12] and/or propylene oxide 10 - a 200-mol addition product (I).

[Claim 4] In the printing ink for metals which changes considering a pigment, resin, and a solvent as a principal component The polyol component which consists of an alkylene oxide addition product (c) of bisphenols, and an alkylene oxide addition product (d) of aliphatic series polyhydric alcohol as this resinous principle, Printing ink for metals which uses the polyester (C) which carboxylic acids (b) are made to react and is obtained, and amino resin (B), and is characterized by the content of (C) to the whole quantity of printing ink being 10 - 70 % of the weight (II).

[Claim 5] Printing ink according to claim 4 whose (C) is polyester of hydroxyl values 30-300 (II).

[Claim 6] Printing ink according to claim 4 or 5 whose content of (c) in this polyol component is 10 - 90 % of the weight (II).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] About the printing ink for metals, in more detail, this invention carries out the wet coat of the aqueous type overprint varnish in the state of an ink sentiment after printing ink, and relates to the printing ink for metals in which the outstanding printability and paint film physical properties are shown in the printing method baked from it.

[0002]

[Description of the Prior Art] Conventionally, the thing (JP,2-24315,A) using the polyester resin which polyester resin is known as printing ink for metals, for example, used rosin alcohol as the indispensable component etc. is proposed.

[0003]

[Problem(s) to be Solved by the Invention] However, in the above-mentioned printing method, with the printing ink which uses conventional polyester resin as a component, diving of HAJIKI of a varnish, aqueous type the fitness over an overprint varnish, i.e., an ink paint film side, and the varnish to the inside of the ink film occurs, consequently gloss or adhesion is missing upwards, and there was a trouble that paint film physical properties, especially a paint film degree of hardness became inadequate.

[0004]

[Means for Solving the Problem] this invention persons are excellent in the fitness (there needs to be neither HAJIKI nor diving) over an aqueous overprint varnish. And the result wholeheartedly examined in order to obtain the printing ink for metals which gives a moderate paint film degree of hardness, HAJIKI can be prevented by using the compound to which alkylene oxide was made to add in order to give compatibility to an aqueous overprint varnish as a polyol component. Moreover, by reducing the viscosity of polyester resin and reducing an unnecessary dilution solvent, it found out that diving could be prevented and this invention was reached.

[0005] Namely, this invention sets (1) resin, a pigment, and a solvent to the printing ink for metals which changes as a principal component. The polyol component which consists of an alkylene oxide addition product (a) of the compound which has two or more active hydrogen as this resinous principle, The polyester (A) and amino resin (B) from carboxylic acids (b) are used. and as the printing ink for metals (I) characterized by the content of (A) to the whole quantity of printing ink being 10 - 70 % of the weight, and a (2) this resinous principle The polyol component which consists of an alkylene oxide addition product (c) of bisphenols, and an alkylene oxide addition product (d) of aliphatic series polyhydric alcohol, It is two of the printing ink for metals (II) which uses the polyester (C) which carboxylic acids (b) are made to react and is obtained, and amino resin (B), and is characterized by the content of (C) to the whole quantity of printing ink being 10 - 70 % of the weight.

[0006] If it has two or more active hydrogen which alkylene oxide can add as a compound which has two or more active hydrogen of (a) in the printing ink (I) of this invention, there will be especially no limit and the compound which has [two or more] a hydroxyl group, the hydroxyl group of phenol nature, a carboxyl group, a hydrogen atom linking directly to a nitrogen atom, etc. will be mentioned.

[0007] as an example -- divalent alcohols (ethylene glycol and propylene glycol --) the alcohols more than trivalent [, such as neopentyl glycol,] (a glycerol --) Butane triol, trimethylol propane, triethanolamine, Sorbitan mono-olate, pentaerythritol, a sorbitol, diglycerol, divalent phenols

(hydroquinone --), such as tripentaerythritol The phenols more than trivalent [, such as a catechol and bisphenol A,] [tris (hydroxyphenyl) methane] etc., a divalent carboxylic acid (oxalic acid, a succinic acid, an alkyl succinic acid, and an adipic acid --) A sebacic acid, a fumaric acid, a maleic acid, a phthalic acid, a terephthalic acid, himic acid, etc., the carboxylic acid more than trivalent (propane tricarboxylic acid and butane tricarboxylic acid --) the univalent 1st class amines (ethylamine --), such as trimellitic acid and pyromellitic acid polyamine (N-methyl ethylene diamine --), such as a butylamine and cyclohexylamine Ethylenediamine, triethylenetetramine, tetraethyl pentamine, Amino alcohol (ethanolamine, diethanolamine, triethanolamine, butyl diethanolamine, the 3-amino -1, 2-propanediol, etc.), such as N-amino piperazine, is mentioned.

[0008] Things desirable [among these] are the alcohols more than trivalent, and are the alcohols more than trivalent [of carbon numbers 3-12] still more preferably.

[0009] (a) adds more than an alkylene oxide (ethylene oxide, propylene oxide, butylene oxide, etc.) kind to the compound which has the two or more above-mentioned active hydrogen, and the 1-1000 mols of the numbers of addition mols of alkylene oxide are usually 10-200 mols preferably.

[0010] As alkylene oxide, ethylene oxide and/or propylene oxide are desirable, and especially concomitant use of a propylene oxide independent or ethylene oxide, and propylene oxide is desirable.

[0011] As this polyol component, polyhydric alcohol, such as the above-mentioned divalent alcohols, alcohols more than trivalent, polyamine, and amino alcohol, may be used together as occasion demands with (a). in this case, the amount of the polyhydric alcohol used -- usually -- 50 or less % of the weight in this polyol component -- desirable -- 20 or less % of the weight -- it is .

[0012] The carboxylic acids of 1 - tetravalence are mentioned as carboxylic acids (b) in this invention. for example, a univalent carboxylic acid (an acetic acid, a propionic acid, stearin acid, and oleic acid --) A benzoic acid, a methyl benzoic acid, a cinnamic acid and a linseed-oil fatty acid, a castor oil fatty acid, Palm oil fatty acid, a palm-kernel-oil fatty acid, a safflower oil fatty acid, a soybean-oil fatty acid, ; divalent carboxylic acids (oxalic acid --), such as natural oil fat fatty acids, such as a tung-oil fatty acid, a rapeseed oil fatty acid, a cotton-seed-oil fatty acid, talloil fatty acid, and a dehydration castor oil fatty acid A succinic acid, an alkyl succinic acid, an adipic acid, a sebacic acid, a fumaric acid, ; trivalent carboxylic acids (propane tricarboxylic acid --), such as a maleic acid, a phthalic acid, a terephthalic acid, and himic acid carboxylic acids (butane tetracarboxylic acid --) of; tetravalence, such as butane tricarboxylic acid and trimellitic acid The ester plasticity derivative of carboxylic acids of; and these [1] - tetravalence, such as pyromellitic acid, (an anhydride, acid halide, methyl ester, glyceride, etc.); such mixture is mentioned to a list.

[0013] A thing desirable as (b) is trivalent or tetravalent a carboxylic acid and its ester plasticity derivative, and especially a desirable thing is trivalent or tetravalent aromatic carboxylic acid and its ester plasticity derivative.

[0014] Using the polyol component which consists more than of an alkylene oxide (addition product a) kind of the compound which has two or more active hydrogen, and more than a (carboxylic-acids b) kind, by the usual approach, the esterification reaction of the polyester (A) is carried out, and it is obtained. Moreover, removing a catalyst component and an alcoholic unreacted component are also removable as occasion demands after a reaction.

[0015] the hydroxyl value of (A) -- usually -- 10-500 -- desirable -- 30-300 -- further -- desirable -- 40-200 -- it is -- the acid number -- usually -- it is ten or less still more preferably 20 or less preferably 50 or less.

[0016] Although the equivalent ratio of the carboxyl group in (b) which constitutes polyester (A), and the hydroxyl group in a polyol component changes with the number of hydroxyl groups in each polyol, and the numbers of carboxyl groups in (b) for example, the equivalent ratio of the carboxyl group in (b) which constitutes (A) when the number of hydroxyl groups of (a) is 3 and the number of carboxyl groups of (b) is 3, and the hydroxyl group in (a) -- usually -- 1: (2-3.5) -- it is 1: (2.5-3.2) preferably.

[0017] The printing ink for metals of this invention changes considering polyester (A), amino resin (B), a pigment, and a solvent as a principal component.

[0018] As amino resin (B), there is especially no limit and it can use guanamine resin (benzoguanamine resin etc.), melamine resin (trimethylolmelamine, hexa methylol melamines, these alkyl ether ghosts, etc.), etc.

[0019] As a pigment, there is especially no limit and it can use inorganic [usual] and an organic

pigment.

[0020] As a solvent, there is especially no limit and polyalkylene oxide besides the usual ink solvents (alkyl ether of saturated hydrocarbon, alkylbenzene, and glycols, diethyl phthalate, etc.) can use it.

[0021] Moreover, use of a dryer, a curing agent, etc. is also possible if needed.

[0022] For polyester (A), 10 - weight % and amino resin (B) are [the content of each component to the printing ink whole quantity / solvents of a pigment] usually 10 - 30% of the weight of range five to 60% of the weight ten to 50% of the weight preferably ten to 70% of the weight.

[0023] The mixed approach of each component does not have especially a limit, and the approach in ordinary use using 3 rolls, a ball mill, etc. can be used.

[0024] If the printing approach of the printing ink for metals of this invention is illustrated, after carrying out dry-relief offset curved surface printing, roll coating of the finishing varnish will be carried out in the state of an ink sentiment, and the approach which can be burned in ink from on the will be mentioned.

[0025] The printing conditions of ink are usually 130 degrees C - 230 degrees C, and time amount is the range for 20 seconds - 20 minutes.

[0026] In the printing ink constituent with which this invention mainly consists of a pigment, resin, and a solvent further The polyol component which consists of an alkylene oxide addition product (c) of bisphenols, and an alkylene oxide addition product (d) of aliphatic series polyhydric alcohol as this resinous principle, It is invention about the printing ink for metals (II) which uses the polyester (C) which carboxylic acids (b) are made to react and is obtained, and amino resin (B), and is characterized by the content of (C) to the whole quantity of printing ink being 10 - 70 % of the weight.

[0027] As bisphenols of (c) in the printing ink (II) of this invention, these derivatives (a styrene ghost, alkylation object, etc.), such as bisphenol A, Bisphenol B, Bisphenol S, and a methylenebis phenol, are mentioned.

[0028] (c) -- bisphenols -- more than an alkylene oxide (ethylene oxide, propylene oxide, butylene oxide, etc.) kind -- adding -- the number of addition mols of alkylene oxide -- usually -- 3-200-mol 1-1000 mols are 3-50 mols more preferably.

[0029] As alkylene oxide which constitutes (c), ethylene oxide and/or propylene oxide are desirable.

[0030] The alkylene oxide addition product (d) of polyhydric alcohol divalent alcohols (ethylene glycol and propylene glycol --) the alcohols more than trivalent [, such as neopentyl glycol,] (a glycerol --) Butane triol, trimethylol propane, triethanolamine, Sorbitan mono-olate, pentaerythritol, a sorbitol, diglycerol, More than a kind is added for alkylene oxide to the amino alcohol (triethanolamine, butyl diethanolamine, etc.) which do not have a hydrogen atom linking directly to a nitrogen atom, such as tripentaerythritol.

[0031] The 1-1000 mols of the numbers of addition mols of the alkylene oxide of (d) are usually 10-200 mols preferably.

[0032] Also as alkylene oxide which constitutes (d), ethylene oxide and/or propylene oxide are desirable, and especially concomitant use of a propylene oxide independent or ethylene oxide, and propylene oxide is desirable.

[0033] the weight ratio of (c)/in a polyol component (d) -- usually -- 5 / 95 - 90/10 -- it is 10 / 90 - 80/20 preferably.

[0034] As this polyol component, polyhydric alcohol, such as the above-mentioned divalent alcohols, alcohols more than trivalent, polyamine, and amino alcohol, may be used together as occasion demands with (c) and (d). In this case, the amount of the polyhydric alcohol used is usually 50 or less % of the weight in this polyol component.

[0035] As carboxylic acids (b), the same carboxylic acids (b) as (I) of this invention are mentioned.

[0036] A thing desirable as (b) is the same as that of what was mentioned as a desirable thing by (I) of this invention.

[0037] The esterification reaction of the polyester (C) is carried out to the polyol component which consists of more than an alkylene oxide (addition product c) kind of the bisphenols which have two or more active hydrogen, and more than an alkylene oxide (addition product d) kind of polyhydric alcohol by the usual approach using carboxylic acids (b), and it is obtained. Moreover, removing a catalyst component and an alcoholic unreacted component are also removable as occasion demands after a reaction.

[0038] the hydroxyl value of (C) -- usually -- 10-500 -- desirable -- 30-300 -- further -- desirable -- 40-200 -- it is -- the acid number -- usually -- it is ten or less still more preferably 20 or less preferably 50 or less.

[0039] although the equivalent ratio of the carboxyl group in (b) which constitutes polyester (C), and the hydroxyl group in this polyol component changes with the number of hydroxyl groups in each polyol, and the numbers of carboxyl groups in (b) -- usually -- 1: (1.5-5) -- it is 1: (2.5-3.5) preferably.

[0040] The printing ink for metals of this invention (II) changes considering polyester (C), amino resin (B), a pigment, and a solvent as a principal component.

[0041] As amino resin (B), a pigment, and a solvent, the same thing as the printing ink (I) of this invention can be used.

[0042] Moreover, use of a dryer, a curing agent, etc. is also possible if needed.

[0043] The content of each component to the printing ink whole quantity, the mixed approach of each component, the printing approach of the printing ink for metals of this invention (II), and the printing conditions of ink are the same as that of the case of the printing ink (I) of this invention.

[0044]

[Example] Hereafter, although an example explains this invention further, this invention is not limited to this. The section in an example is the weight section.

[0045] The propylene oxide addition product (molecular weight = 700) 700 section (one mol) of example of manufacture 1 trimethylol propane and the trimellitic anhydride 63.4 section (0.33 mols) were esterified with the conventional method, and the transparent viscous liquid-like resin (resin A-1) of a hydroxyl value 153 and the acid number 3.7 was obtained.

[0046] The ethylene oxide / propylene oxide random addition product (weight ratio 30/70, molecular weight = 1000) 1000 section (one mol) of example of manufacture 2 glycerol, the neopentyl glycol 104 section (one mol) and the trimethylol propane 134 section (one mol), and the trimellitic anhydride 192 section (one mol) were esterified with the conventional method, and the transparent viscous liquid-like resin (resin A-2) of a hydroxyl value 59 and the acid number 4.2 was obtained.

[0047] The propylene oxide addition product (molecular weight = 1000) 1000 section (one mol) of example of manufacture 3 pentaerythritol and the pyromellitic dianhydride 55 section (0.25 mols) were esterified with the conventional method, and the transparent viscous liquid-like resin (resin A-3) of a hydroxyl value 166 and the acid number 4.9 was obtained.

[0048] the propylene oxide addition product (molecular weight = 460) 920 section (two mols) of example of manufacture 4 bisphenol A -- and -- ** -- the ethylene oxide / propylene oxide random addition product (weight ratio 30/70, molecular weight = 700) 700 section (one mol) of trimethylol propane and the trimellitic anhydride 192 section (one mol) were esterified with the conventional method, and the transparent viscous liquid-like resin (resin C-1) of a hydroxyl value 172 and the acid number 3.7 was obtained.

[0049] The ethylene oxide addition product (molecular weight = 580) 1450 section (2.5 mols) of example of manufacture 5 bisphenol A and the propylene oxide addition product (molecular weight = 1000) 500 section (0.5 mols) of a glycerol, and the trimellitic anhydride 192 section (one mol) were esterified with the conventional method, and the transparent viscous liquid-like resin (resin C-2) of a hydroxyl value 94 and the acid number 2.0 was obtained.

[0050] The ethylene oxide / propylene oxide random addition product (weight ratio 30/70, molecular weight = 1000) 1000 section (one mol) of example of manufacture 6 bisphenol A, the propylene oxide addition product (molecular weight = 700) 700 section (one mol) of pentaerythritol, the neopentyl glycol 104 section (one mol) and the trimethylol propane 134 section (one mol), and the pyromellitic dianhydride 218 section (one mol) were esterified with the conventional method, and the transparent viscous liquid-like resin (resin C-3) of a hydroxyl value 125 and the acid number 5.4 was obtained.

[0051] The example of manufacture 7 neopentyl-glycol 170 section, the trimethylol propane 110 section, the adipic-acid 170 section, and the isophthalic acid 200 section were esterified with the conventional method by having made the dibutyltin dilaurate 1.9 section into the catalyst, and the transparent viscous liquid-like resin (comparison resin D-1) of a hydroxyl value 91 and the acid number 5.9 was obtained.

[0052] Examples 1-6 and example of comparison 1 resin A-1 to A-3, C-1-3, and D-1 the 40 sections each are used. To each, the diethylene-glycol monobutyl ether 15 section, the titanium oxide 40 section,

the hexa methylol melamine (Mitsui Toatsu Chemicals Cymel 300) 15 section -- adding -- subsequently -- each -- 3 roll mills -- using -- ink ---izing -- ink A' -1 - A -- '-3 (examples 1-3), C' -1 - C -- '-3 (examples 4-6) and D' -1 (example 1 of a comparison) was obtained.

[0053] It is made to be the same as that of examples 1-6 and the example 1 of a comparison except having used alkylbenzene (alkene N56N made from the Nippon Oil chemistry) instead of examples 7-12 and the example of comparison 2 diethylene-glycol monobutyl ether. ink [from resin A-1] A'' -1 (example 7) -- the same -- ink A' -- '-2 - A' -- '-3 (examples 8-9), C' -- '-4 - C' -- '-6 (examples 10-12), D'' -1 (example 2 of a comparison) was obtained, respectively.

[0054] The ink obtained in the example of a trial, the example examples 1-12 of a comparative study, and the examples 1-2 of a comparison is used. It prints by the dry-relief offset method with an aluminum 2 piece can. The aquosity acrylic resin (Mitsui Toatsu Chemicals ARUMA tex WA41) 60 section, The deionized water 60 section, the water-soluble benzoguanamine resin (Mitsui Toatsu Chemicals Cymel 1123) 15 section, 200 degrees C after overprinting on the whole surface the aquosity overprint varnish which consists of the butyl-cellosolve 10 section, and printing during 2 minutes -- carrying out -- paintwork (HAJIKI, gloss) and a paint film degree of hardness -- it evaluated. A result is shown in Table 1.

[0055]

[Table 1]

	インキ	ハジキ	光沢	塗膜硬度
	インキA' -1	○	○	4H
試	インキA' -2	○	○	4H
	インキA' -3	○	○	5H
	インキA' ' -1	○	○	4H
	インキA' ' -2	○	○	5H
験	インキA' ' -3	○	○	4H
	インキC' -1	○	○	6H
	インキC' -2	○	○	6H
例	インキC' -3	○	○	7H
	インキC' ' -1	○	○	6H
	インキC' ' -2	○	○	6H
	インキC' ' -3	○	○	7H
比 試	インキD' -1	△	×	3H
較 験				
例	インキD' ' -2	×	△	3H

[0056] - gloss, HAJIKI; (Note) The paint film was viewed, and when good, in the case of O, case [of normal level] **, and use improper level, it considered as x, and was shown.

- Paint film degree of hardness ; JIS was followed and the pencil degree of hardness of a paint film showed.

[0057]

[Effect of the Invention] As mentioned above, since diving of HAJIKI of the varnish in an ink paint film side or the varnish to the inside of the ink film does not occur to an aquosity type overprint varnish in the printing method which carries out the wet coat of the aquosity type overprint varnish in the state of the ink sentiment after printing, and bakes ink from it, when it has sufficient fitness, the printing ink for metals of this invention (I), and (II) give the outstanding gloss and the outstanding paint film degree of hardness, as the example etc. showed.

[Translation done.]